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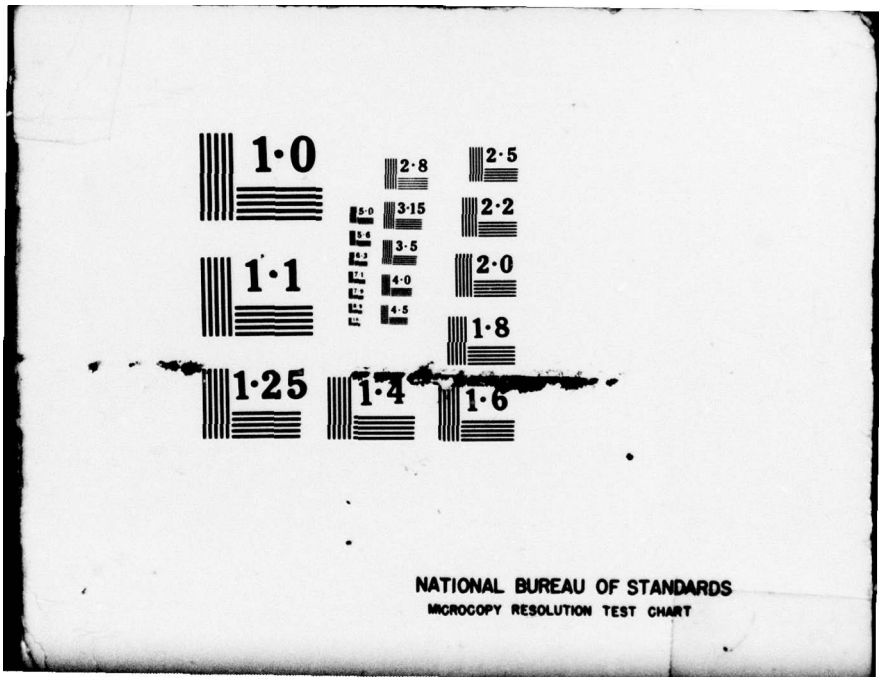
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Final Report on the Work Sponsored by AFOSR Grant No. 75-2822

Principal Investigator: P. Davidovits - Boston College

Abstract

Techniques have been developed for the study of highly exoergic reactions of boron and carbon atoms. Merged flow, diffusion and single collision experiments were performed to measure total reaction cross sections, chemiluminescence cross sections and population distributions in the electronically excited states of reaction products. The basic purpose of these studies was to gather a body of systematic data in order to understand the reaction mechanism and the production of electronically excited states for this important class of non-metal atom reactions. Total cross sections were measured for the reaction of carbon atoms with lead oxide (PbO). The cross section is $20\mathring{A}^2$. The total reaction cross sections of boron atoms with O_2 and SO_2 are respectively $1\mathring{A}^2$ and $0.8\mathring{A}^2$. The cross sections for the reaction of boron with N_2O and CO_2 is less than $0.08\mathring{A}^2$. The cross sections for the production of electronically excited states of reaction products were determined for the reactions of carbon atoms with PbO and boron atoms with O_2, CsF and RbF. These values are respectively $5\mathring{A}^2$, $0.05\mathring{A}^2$, $3\mathring{A}^2$ and $7\mathring{A}^2$. The population distribution in the electronically excited product states was determined for the reactions of carbon atoms with PbO, and boron atoms with CsF, RbF, KF, NaF, and O_2. Population inversion between electronically excited states was observed in several reactions.

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1. INTRODUCTION

The study of exoergic gas phase reactions has been an important area of research for many years. Recently, there has been an increased interest in these reactions motivated in part by developments in the fields of plasma chemistry, laser induced chemistry, magnetohydrodynamics (MHD) and chemical lasers. In all these areas exoergic reactions play an important role and more basic information about them would be useful. In the field of laser induced chemistry, for example one wants to know which quantum states are most likely to react. In what ways does vibrational excitation of the reactant molecules effect the course of the reaction? In choosing candidates for chemical lasers it would be useful to know which parameters influence the distribution of energy released in exoergic reactions. Under what conditions are the products electronically and vibrationally excited? Which quantum states are preferentially produced in the reaction, or more specifically, can population inversion be predicted?

Over the past few years experimental techniques have been developed which permit detailed studies of chemical reactions geared toward answering these types of fundamental questions.

Many basic questions about chemical reactions however, still remain unanswered. This is especially the case for highly exoergic reactions of non-metal atoms where the energy is sufficient to produce electronically excited products. Very few studies have been conducted to measure reaction cross sections or the distribution of chemical energy in the reaction. As a result very little is known about the mechanism that governs such reactions. Yet this is an imporatant group of reactions which includes the reactions

of atoms such as boron, carbon, sulfur, nitrogen etc. Systematic studies were needed in this area. Clearly, relatively simple reactions are preferred for such studies since they provide less ambiguous experimental results and are more amenable to theoretical modeling.

The gas phase reactions of boron and carbon atoms lend themselves to such a systematic study. Some of the simple gas phase reactions of boron and carbon atoms are among the most exoergic found in nature. In the formation of a carbon-oxygen bond for example, the energy released is about 11 eV which is the highest amount of energy obtainable from an atom-atom bond. The energies released in the formation of B-F and B-O bonds are 8 eV and 7.4 eV respectively.

The reactions of these atoms are relatively simple and yet they exhibit a wide range of interesting phenomena. Several sets of homologous reactions are available for study which should yield systematic results amenable to theoretical modeling.

The aim of the research sponsored by the grant no AFOSR 75-2822 was to study simple reactions of these atoms in which the exoergicity is sufficient to produce electronically excited products. The following types of reactions have been studied.

1. $B + MF \rightarrow BF + M^*$ e.g. $B + CsF \rightarrow BF + Cs^*$
2. $B + RO \rightarrow BO^* + R$ e.g. $B + N_2O \rightarrow BO + N_2$
3. $C + MO \rightarrow CO + M^*$ e.g. $C + PbO \rightarrow CO + Pb^*$

Boron and carbon are highly refractory materials, therefore the first task of the project was to develop convenient sources of these atoms for the required experiments. This phase of the project is described in sectior 1.

Reactions rates and the distribution of electronically excited states of the reaction products have been measured for several reactions. Both merged flow and single collision beam experiments were conducted. The results are described briefly in section 2, 3 and 4 of this report. A more detailed description is found in the publications listed in section 6. Conclusions and suggested direction for future work are discussed briefly in section 5.

1. Production of Boron and Carbon Atoms

One of the difficulties in the study of elemental boron and carbon reactions is the production of an adequate density of atoms. We have pursued three methods of producing boron and carbon atoms.

(a) Dissociation of a boron or carbon containing gas with an microwave discharge.

(b) Thermal vaporization at about 2000°C.

(c) Pulsed laser heating.

(a) Microwave discharge production of boron and carbon

We did extensive experiments on the production of boron in a microwave discharge. There are many boron containing compounds which are gases at room temperature (e.g. BCl_3, BF_3, B_2H_6, etc.) and most of them can be fragmented to produce elemental boron. The boron atoms however tend to recombine very rapidly with the reactive fragments in the discharge. It is therefore necessary to dilute the discharge with an inert gas such as helium. We monitored the atomic boron above the discharge source by observing the absorption of boron resonance light passing through the region. We obtained the best results with a discharge of 1% B_2H_6

in helium. We estimate that the density of boron above the discharge is about $5 \times 10^{10}/cm^3$. In the reaction zone the density is about $10^9/cm^3$. A similar technique was used in our experiments with carbon atoms.

Carbon atoms were produced in a flowing microwave discharge of 1% CO in 99% He. The density of carbon atoms in the reaction region was monitored by observing the absorption of 2478 Å light produced in a discharge lamp containing 14 torr He and 50 torr CO. This wavelength monitors the density of the metastable carbon atoms. The total density of carbon is estimated by weighing the carbon deposited on a glass slide over a given period of time. Depending on the distance of the microwave discharge from the reaction region, the density of metastable atoms was as high as $10^{10}/cm^3$ while the total carbon density was about $10^{14}/cm^3$.

The microwave discharge was produced by a Raytheon power source which has been modified so that it can be used inside the vacuum chamber while being tuned from the outside. This entailed the design and construction of a new long cavity with the extended tuning stub isolated from the vacuum.

(b) A knudsen cell apparatus was assembled in which boron contained in tantalum of tungsten crucibles was heated by electron bombardment. Temperatures up to 2500°C have been reached. This source is now used in a beam apparatus.

(c) It is well known that an intense laser pulse focused on a boron or carbon surface will vaporize the surface. Unfortunately the vapor contains not only ground state atoms but also polymers, excited species and ions. We have observed the production of these species in our initial experiments. In order to perform controlled experiments with a laser produced vapor one must be able to character-

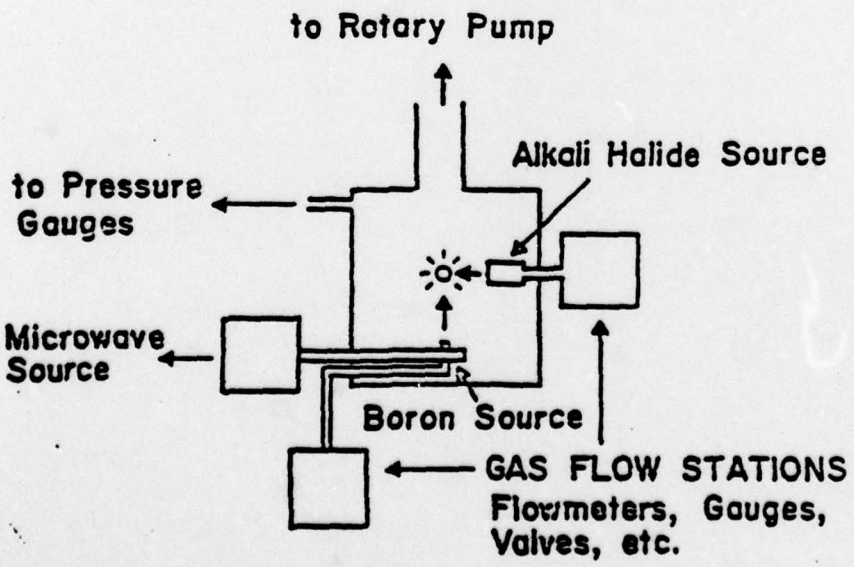
ize its composition and control it so that the effects of the various components in the vapor can be separated.

Before continuing our studies of laser boron and carbon production we decided to start a project designed to answer basic questions in connection with laser vaporization. The experiments are more easily interpreted with a metal surface such as sodium and thallium and therefore we chose to study first these surfaces. Those experiments which are now completed point out the limitations of pulsed laser vaporization in the production of neutral atoms from refractory materials such as boron and carbon. The results of this work have been published in the Journal of Applied Physics. (Publication 2 section ( ).

2. Merged Flow Studies

We have completed merged flow studies of the gas phase reactions of boron with CsF, RbF, KF and NaF. A simplified drawing of the apparatus is shown in figure 1. Atomic boron was produced in a

Fig. 1



microwave discharge of a B_2H-Helium mixture. The densities of ground state boron and alkali atoms produced in the reaction were determined by absorption measurements. Light from excited alkali atoms in the reaction region was recorded and the excited state population densities were calculated. Population inversion was observed between some of the excited states. Our evidence indicates that alkali atoms (M) in the first excited P states are produced primarily in the direct reaction B + MF $\rightarrow$ BF + M*. Several additional processes contribute to the production of higher excited states. This work has been published in J. Chem. Phys. 65, 5373 (Dec. 15, 1976). Publication 1 section 6.

A somewhat modified version of the apparatus in figure 1 was used to study the reaction C + PbO $\longrightarrow$ CO + Pb*. Chemiluminescence was observed from the excited lead atoms. Population distribution from some of the excited states was determined. The total cross section for the reaction and the cross section for the production of electronically excited states are estimated to be 20 and 5 Å^2 respectively.

Inversion is observed between a number of excited states. Various checks were performed to ascertain the source of excitation. For example, the experiment was conducted with Pb atoms replacing the PbO molecules. The light from the reaction zone was negligible, showing that direct excitation of lead atoms was not significant. The emitted light was also negligible when CO was replaced by N_2 and NO. This work was accepted for publication in Chem. Phys. Letters (publication 3 section 6).

3. Diffusion Technique for the Measurement of total Cross Sections

We used a diffusion technique to measure the total reaction

cross section for boron atoms. The boron produced by the microwave discharge was admitted through a nozzle into a chamber where it mixed diffusively with the reactant at a known density. Under proper conditions achieved in our experiment the rate constant k is given by

$$k = \frac{(\ell n\ n_o r_o / n_1 R)^2 D}{(R - r_o)^2 n'} \qquad (cm^3 mole^{-1} sec^{-1})$$

n_o: initial density of boron (normally at the nozzle)

n_1: density of boron at a distance R from the nozzle

D: Diffusion coefficient of boron in the gas mixture (in $cm^2 sec^{-1}$)

r_o: radius of the nozzle

n': density in mole/cm^3

The density of boron in these experiments was determined by measuring the boron resonance light absorption. We have measured the rate constant for the reaction of boron atoms with O_2, SO_2, N_2O and CO_2. The cross sections for these reactions are for O_2 1Å^2, for SO_2 0.8Å^2. The reaction rates with N_2O and CO_2 are very small. An upper limit for the cross section has been established to be less than 0.08Å^2. A manuscript describing this work is in preparation (Publication 5 section 6).

4. Single Collision Beam Experiments

A beam apparatus was constructed for the single collision studies of boron reactions. A simplified sketch of the beam apparatus is shown in figure 2. The various gauges, light baffles, heat shields and shutters are not shown. The crucible which contains solid boron was heated by electron bombardment. Crucibles are machined from tantalum or from tungsten and are lined

with a carbon liner. The material can be heated up to about 2500 C.

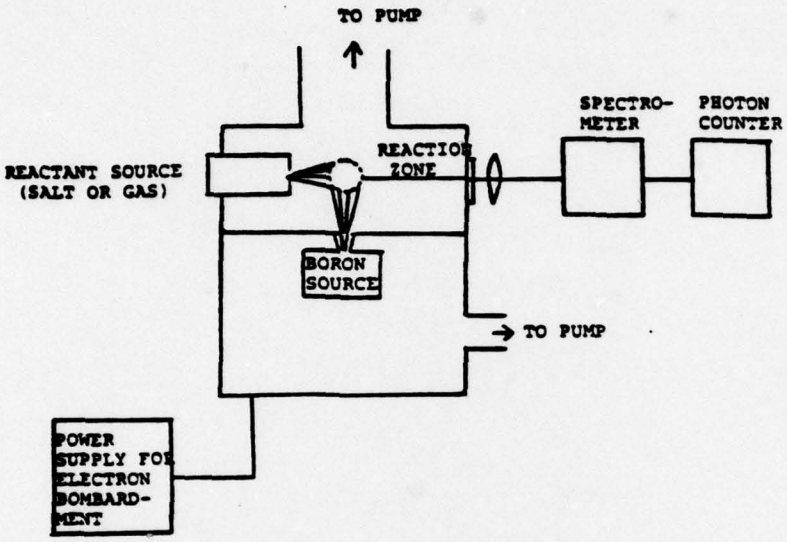


Fig. 2

The method of production of the reactant molecules depends on the reaction to be studied. For the reactions with the metal oxides and fluorides the beams were obtained from an oven made of stainless steel wound with insulated heater wire. The oxide or fluoride were contained in a stainless steel boat inside a stainless steel cylinder with a 1 mm exit hole. Gas phase reactants were admitted into the reaction zone through a gas handling system made of non-corrosive materials. The crucible section and the reaction section were pumped by two inch and three inch diffusion pumps respectively.

The present beam system is a relatively small one. A much larger apparatus is now under construction. Two 18 inch joint

stainless steel chambers are being built. They will be pumped by a 10 inch diffusion pump which has already been acquired. This system will provide higher beam densities and will be suitable for future triple beam experiments.

In the present system the boron beam density in the reaction zone was approximately $5 \times 10^{8} cm^{-3}$. The density of the reactant molecules was in the range $8 \times 10^{12} cm^{-3}$. In the new system these densities will be significantly higher.

The chemiluminescence from the reaction zone was detected by a spectrometer-photomultiplier-photon counter combination. The photon counter was manufactured by Ortec. The photomultiplier was cryogenically cooled. An elaborate light shielding arrangement blocked the stray light from the thermally heated components and allowed the detection of signals as low as five counts per second. The detection apparatus has been calibrated to measure absolute photon yields.

With our present system the five photons per second detection limit corresponds to about 10^{6} photons emitted per second in the reaction zone. Since the volume of the observed reactions zone is $0.15 cm^{3}$ this corresponds to 6.7×10^{6} photons per second per cm^{3}. (The detection efficiency including the solid angle, spectrometer and photomultiplier is 6.05×10^{-6}).

Single collision experiments have been completed for the reaction B+CsF, B+RbF, $B+O_2$ and $B+N_2O$.

The cross sections for the production of excited states are about $3\mathring{A}^2$ for Cs and $7\mathring{A}^2$ for Rb. Population inversions in cesium were observed between the 8S 7P, 8S 6P, 6D 6P states.

Since the potential curves and the intensity factors for the BO molecule are well known, the nascent vibrational population distribution in the excited $A^2\pi$ state can be determined from these spectra. With all the relevant parameters calibrated the absolute value of the cross section for the production of this state can also be calculated. This value is 0.05Å^2. Chemiluminescence was not observed in the $B+N_2O$ reaction. The details of this experiment are described in publication 4 section 6.

5. Conclusions:

We have developed techniques for the study of boron and carbon atom reactions. One carbon atom reaction and several boron atom reactions have studied. Total reaction cross sections and cross sections for the production of electronically excited states have been determined. While certain patterns are beginning to emerge a number of other reactions will have to be studied before a model for these reactions can be proposed. Such studies are now in progress. One surprising result of our experiments is the low reactivity of boron with N_2O. This molecule is highly reactive with metals and its reaction with boron is potentially highly exoergic. The reason for its relative inertness with boron is not yet understood. Further studies with molecules of various structures should provide the answer.

6. Publications Resulting from the Grant Sponsored Research

1. "Chemiluminescence from the Gas Phase Reaction of Atomic Boron With the Alkali Metal Fluorides", U.C. Sridharan, D.L. McFadden and P. Davidovits, J. Chem. Phys. 65, 5373 (1976).

2. "Production of Neutral Atoms by Pulsed Laser Heating", A. Prengel, J. DeHaven, E.J. Johnson and P. Davidovits, J. Appl. Phys., 48, 3551 (1977).

3. "Chemiluminescence from the Gas Phase Reactions of Atomic Carbon with PbO", U.C. Sridharan, T.G. DiGiuseppe, D.L. McFadden and P. Davidovits, Accepted for publication in Chem. Phys. Letters,

4. "Chemiluminescence Studies of Boron Atom Reactions with O_2 and N_2O, A. Brzychcy, J. DeHaven, A.T. Prengel and P. Davidovits, Accepted for publication Chem. Phys. Letters.

5. "Cross Sections for the Reaction of Boron Atoms with O_2, SO_2, N_2O and CO_2", U.C. Sridharan, T.G. DiGiuseppe, D.L. McFadden and P. Davidovits, Manuscript in preparation for submission to J. Chem. Phys.

6. "Beam Studies of the Reaction of Boron Atoms with the Alkali Metal Fluorides", J. DeHaven, A. Brzychcy and P. Davidovits, Manuscript in preparation for submission to J. Chem. Phys.

7. List of Personnel

Faculty

P. Davidovits, Principal Investigator, Professor of Chemistry

D.L. McFadden, Associate Professor

Post Doctoral Fellows

E.J. Johnson, Ph.D.

A.T. Prengel, Ph.D.

Graduate Students

Mr. U.C. Sridharan*

Mr. J. DeHaven

Mr. T. DiGiuseppi

Ms. A. Brzychcy**

*Ph.D. research completed. Theses in preparation.

**M.S. research work completed. Theses in preparation.

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140 Commonwealth Avenue
Chestnut Hill, MA 02167

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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population distributions in the electronically excited states of reaction products. The basic purpose of these studies was to gather a body of systematic data in order to understand the reaction mechanism and the production of electronically excited states for this important class of non-metal atom reactions. Total cross sections were measured for the reaction of carbon atoms with lead oxide (PbO). The cross section is 20Å^2. The total reaction cross sections of boron atoms with O_2 and SO_2 are respectively 1Å^2 and 0.8Å^2. The cross sections for the reaction of boron with N_2O and CO_2 is less than 0.08Å^2. The cross sections for the production of electronically excited states of reaction products were determined for the reactions of carbon atoms with PbO and boron atoms with O_2, CsF and RbF. These values are respectively 5Å^2, 0.05Å^2, 3Å^2 and 7Å^2. The population distribution in the electronically excited product states was determined for the reactions of carbon atoms with PbO, and boron atoms with CsF,RbF, KF, NaF, and O_2. Population inversion between electronically excited states was observed in several reactions.